ON THE SEPARATION OF THE LEAST VOLATILE GASES OF ATMOSPHERIC AIR, AND THEIR SPECTRA.[1]

THE separation of these gases from each other was effected by collecting them in a bulb in the solid state and allowing the solid gradually to evaporate at as low a temperature as possible, while the vapour was continually pumped away with a mercurial pump. Between the bulb containing the solidified gases and the pump a sparking tube was interposed, where the spectrum emitted by the vapour under the influence of an electric discharge was from time to time observed.

The success of the operation of separating the gases which boil at different temperatures depends on keeping the temperature of the solid mass as low as possible, as will be seen from the following consideration :—

The pressure, p, of a gas G, above the same material in the liquid state, at temperature T, is given approximately by the formula

$$\log p = A - \frac{B}{T},$$

where A and B are constants for the same material. For some other gas G′ the formula will be

$$\log p_1 = A_1 - \frac{B_1}{T},$$

and

$$\log \frac{p}{p_1} = A - A_1 + \frac{B_1 - B}{T}.$$

Now for argon, krypton and xenon, respectively, the values of A are 6·782, 6·972 and 6·963, and those of B are 339, 496·3 and 669·2 ; and for these and many other substances $A - A_1$ is always a small quantity, while $\frac{B_1 - B}{T}$ is considerable and increases as T diminishes. Hence the ratio of p to p_1 increases rapidly as T diminishes, and by evaporating the gases always from the solid state and keeping the solid at as low a temperature as possible, the gas first coming off consists in by far the greatest part of that which has the lowest boiling point, and is succeeded, with comparative abruptness, by the gas which has the next higher boiling point. So abrupt indeed is the succession that the nitrogen is almost completely removed before the argon makes its appearance, and the necessity for removing the nitrogen by sparking with oxygen almost wholly avoided. The change from one gas to another is easily detected by examining the spectrum in the sparking tube, and the reservoirs into which the gases are pumped can be changed when the spectrum changes and the fractions separately stored.

The general sequence of spectra, omitting those of nitrogen, hydrogen and compounds of carbon, which were never entirely removed by the process of distillation alone, was as follows : The spectrum of argon was first noticed in succession to nitrogen, and then as the distillation proceeded the brightest rays, green and yellow, of krypton appeared, and then the intensity of the argon spectrum waned, and it gave way to that of krypton until, as predicted by Runge, when a Leyden jar was in the circuit, the capillary part of the sparking tube had a magnificent blue colour, while the wide ends were bright pale yellow. Without a jar the tube was nearly white in the capillary part, and yellow about the poles. As the distillation proceeded, the temperature of the vessel containing the solid mixture being allowed to rise slowly, the brightest of the xenon rays began to appear, namely, the green rays about λ 5420, 5292 and 4922, and then the krypton rays soon died out and were superseded by the xenon rays. At this stage the capillary part of the sparking tube is, with a jar in circuit, a brilliant green, and is still green, though less brilliant, without the jar. The xenon formed the final fraction distilled.

The authors give a long list of the approximate wave-lengths of rays they have observed to be emitted by xenon and krypton under the influence of electric discharge.

The variation of the spectra of both xenon and krypton with variation in the character of the electric discharge is very striking, and has already been the subject of remark, in the case of krypton, by Runge, who has compared krypton with argon in its sensitiveness to changes in the electric discharge. Runge distinguishes krypton rays which are visible without a jar and those which are only visible with a jar discharge. The difference in the intensity of certain rays, according as the discharge is continuous or oscillatory, is no doubt very marked, but, with rare exceptions, the authors have found that the rays which are intensified by the oscillatory discharge can be seen with a continuous discharge when the slit of the spectroscope is wide. Runge used a grating, whereas they have, for the sake of more light, used a prism spectroscope throughout, and were therefore able to observe many more rays than he.

There is one very remarkable change in the xenon spectrum produced by the introduction of a jar into the circuit. Without the jar xenon gives two bright green rays at about λ 4917 and λ 4924, but on putting a jar into the circuit they are replaced by a single still stronger ray at about λ 4922. In no other case have the authors noticed a change so striking as this on merely changing the character of the discharge. It is noteworthy that the ray λ 4922 is close to a well-known helium ray, but other helium rays were not seen in the same spectrum. Changes of the spectrum by the introduction of a jar into the circuit are, however, the rule rather than the exception, and there are changes in the spectrum of krypton which seem to depend on other circumstances. Of many tubes filled with krypton in the manner above indicated, some give with no jar the green ray λ 5571, the yellow ray λ 5871 and the red ray λ 7600 very bright, while other rays are very few, and those few barely visible. Putting a jar into the circuit makes very little difference ; the three rays above mentioned remain much the brightest, nearly, though not quite, so bright as before, and the blue rays, so conspicuous in other tubes, though strengthened by the use of the jar, are still very weak. In other tubes the extreme red ray is invisible, the rays at λ 5571 and 5871 absolutely, as well as relatively, much feebler, while the strong blue rays are bright, even brighter than the green and yellow rays above named. In one tube the blue rays could be seen, though not the others. This looks very much as if two different gases were involved, but the authors have not been able to assure themselves of that. The case seems nearly parallel with that of hydrogen. There are some hydrogen tubes which show the second spectrum of hydrogen very bright, and others which show only the first spectrum ; the second spectrum is enfeebled or extinguished by introducing a jar into the circuit, while the first spectrum is strengthened ; and the conditions which determine the appearance of the ultra-violet series of hydrogen rays have not yet been satisfactorily made out.

It is to be noted that putting the jar out of circuit does not in general immediately reduce the brightness of the rays which are strengthened by the jar discharge. Their intensity fades gradually, and is generally revived, more or less, by reversing the direction of the current, but this revival gets less marked at each reversal until the intensity reaches its minimum. The rays strengthened by the jar discharge also sometimes appear bright, without a jar, on first passing the spark when the electrodes are cold, and fade when the electrodes get hot, reappearing when the tube has cooled again. Moreover, if the discharge be continued without a jar, the resistance in the krypton tubes increases rather rapidly, the tube becomes much less luminous and finally refuses to pass the spark. With an oscillatory discharge the passage of the spark and the brightness of the rays are much more persistent. This seems to point to some action at the electrodes which is more marked in the case of krypton than in that of xenon.

The xenon spectrum is characterised by a group of four conspicuous orange rays of about equal intensities, a group of very bright green rays of which two are especially conspicuous, and several very bright blue rays. The list of xenon rays published by Erdmann does not present any close agreement with that of the authors except as to the strongest green lines. The number of xenon rays observed is very considerable, and some of them lie very near to rays of the second spectrum of hydrogen, but inasmuch as these rays are more conspicuous with a jar in circuit than without, which is not the character of the second spectrum of hydrogen, and as, moreover, many of the brightest of the hydrogen rays are absent from the spectrum of the tubes, the authors conclude that these rays are not due to hydrogen.

Certain rays, tabulated separately, have been as yet observed in only one xenon tube ; they include a very strong ultra-violet ray of unknown origin, and due either to some substance other than xenon or to some condition of the tube which has not been repeated in the other tubes.

[1] Abridged from a paper by Prof. G. D. Liveing, F.R.S., and Prof. J. Dewar, F.R.S., read before the Royal Society on June 20.

The authors' krypton rays agree tolerably closely with Runge's list, but outnumber his very considerably, as might be expected when prisms were used instead of a grating. The authors think that the krypton used by Runge must have contained some xenon, and that the rays for which he gives the wave-lengths 5419·38, 5292·37 and 4844·58 were really due to xenon, as they are three of the strongest rays emitted by their xenon tubes, and are weak in, and in some cases absent from, the spectra of their krypton tubes.

Appended to the paper are tables showing wave-lengths of xenon and krypton lines to four figures.

UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

THE University of St. Andrews has received information that a legacy of 4000*l.* has been left to it by the late Miss Malcolm for the establishment of medical bursaries and scholarships.

ACTING on the suggestion made by Mr. Chamberlain, the general purposes committee of the Birmingham City Council has resolved to recommend the Council to make a grant to the Birmingham University of the proceeds of a halfpenny rate. This will provide an annual sum of 5000*l.*

THE Agent General for New South Wales intimates that applications are invited from gentlemen qualified to fill the chair of pathology in the University of Sydney. Particulars may be obtained from the Agent General for New South Wales, 9, Victoria Street, London, S.W.

THE Technical Education Board of the London County Council has directed the higher education subcommittee to inquire and report (*a*) as to the need and present provision for special training of an advanced kind in connection with the application of science (especially chemistry and electricity) to industry; (*b*) as to what, if any, developments are needed to secure efficient training in these subjects for senior county scholars and other advanced students who desire to qualify themselves to take leading positions in scientific industries. The Board has arranged to make a grant of 10,000*l.* a year to the University of London, and is thus directly interested in the development of advanced scientific instruction in London.

SCIENTIFIC SERIAL.

American Journal of Mathematics, vol. xxiii. No. 3.—Geometry on the cubic scroll of the second kind, by F. C. Ferry, is the conclusion (34 pp.) of a paper commenced in the last number.—Congruent reductions of bilinear forms, by T. J. I'A. Bromwich, contains an account and a slight extension of a method due to Kronecker (*Gesamm. Werke*, Bd. i. p. 349). This method was employed in the first place for the reduction of two quadratic forms. In the present paper it is applied to four cases of reductions, viz. (1) two symmetric forms (the same as Kronecker's case); (2) a symmetric and an alternate form; (3) two alternate forms; and (4) two Hermite's forms. In cases (1)-(3) the substitutions are congruent, while in (4) they are conjugate imaginaries. Mr. Bromwich gives a list of the principal papers which deal with the problems he has considered in his article. On the imprimitive substitution groups of degree fifteen and the primitive substitution groups of degree eighteen, by E. Norton Martin, was presented, in abstract and in a slightly different form, at the summer meeting of the American Mathematical Society in 1899. Herein he has added two new groups to his original list, viz. the groups with five systems of imprimitivity simply isomorphic to the alternating and symmetric groups of degree five, and he mentions that Dr. Kuhn reported at the February (1900) meeting of the Society that he had carried the investigation further by adding twenty-eight to the seventy groups found by Mr. Martin. The list even now does not claim to be absolutely complete, since omissions are always possible. A somewhat long list of recent papers on the subject is appended to the article.—Removal of any two terms from a binary quantic by linear transformations, by Bessie G. Morrison, discusses these linear transformations and gives applications to the non-singular cubic, quartic, quintic and sextic.

SOCIETIES AND ACADEMIES.

LONDON.

Geological Society, June 19.—Mr. J. J. H. Teall, V.P.R.S., president, in the chair.—On the use of a geological datum, by Mr. Beeby Thompson. A proper interpretation of geological phenomena frequently requires that allowance shall be made for differential earth-movements that have taken place since the period under consideration. Present differences of level in rocks of the same age may be due to actual differences in depth of the sea-floor on which they were deposited; but they may also be the result of subsequent differential earth-movements. The rock selected as a datum should combine as far as possible the following characteristics:—It should be thin, of considerable horizontal extension, having similarity in physical characters and palæontological contents over a large area, and situated as near as possible, in vertical sequence, to the reference-deposit. In Northamptonshire three formations meet these requirements—the Rhætic Beds, the Marlstone Rock-bed and the Cornbrash. The author applies the Marlstone Rock-bed as a datum to the study of the five chief deep explorations in Northamptonshire, with the following results:—While the old land-surface (below the Trias) now varies in height by more than 250 feet, the variation in thickness of the rocks between it and the Middle Lias only reaches 56½ feet; and although the old land-surface is actually lowest where the Rhætic rocks have not been detected, when compared with the position of the Marlstone it is found to be the highest. The further application of the same method enables the author to recognise Rhætic rocks at Northampton, to correct the record of the Kingsthorpe shaft, and to explain the presence of Triassic saline water in the Marlstone. A revised section of the Kingsthorpe shaft is given. Another point proved is that a general levelling-up process was going on just before the beginning of the Lower Liassic Period, and another at the close of the Middle Liassic Period.—On intrusive, tuff-like, igneous rocks and breccias in Ireland, by Messrs. James R. Kilroe and Alexander McHenry.—Many fragmental igneous rocks, although resembling tuffs, cannot be regarded as ejectamenta on account of their character and mode of occurrence in the field. A series of sections is exhibited to illustrate how tuff-like masses invade black slate of Llandeilo age in the South-east of Ireland, generally adhering to the direction of bedding, but frequently cutting across it and detaching numerous pieces from the slate, which are more abundant near the margins of the intrusion than elsewhere.

PARIS.

Academy of Sciences, July 8.—M. Fouqué in the chair.—On new derivatives of benzylcamphor and benzylidenecamphor, by MM. A. Haller and J. Minguin. In continuation of previous researches it is now shown that the unsaturated acid, $C_6H_5-CH=CH\cdot C_8H_{14}\cdot CO_2H$, obtained by the action of hydrobromic acid on benzylidenecamphor, or by treating bromobenzylcamphor with alcoholic potash or ammonia, combines with a molecule of hydrogen bromide to form phenylbromohomocampholic acid, which, when warmed with hydrobromic acid in acetic acid solution, loses bromine and yields the corresponding hydroxy-acid. The action of bromine on dextrobenzylcamphor results in the formation of two stereoisomeric bromobenzylcamphors which yield benzylidenecamphor on treatment with alcoholic potash. Further bromination of benzylcamphor gives rise to unstable dibromo-derivatives which are converted by the action of potash into ortho- and para-bromobenzylidenecamphors; the para-compound forms bromophenylhydroxyhomocampholic acid on treatment with hydrobromic acid at 100°.—Osmotic pressure and its *rôle* as a protection from cold in the living cell, by M. D'Arsonval. At the low temperature of liquid air animal and vegetable tissues in general become extremely hard and friable, whereas the vitality of yeast and various pathogenic micro-organisms is not impaired even by several weeks' exposure to cold. In explanation of this fact it is suggested that the solidification of such minute cells is prevented by the enormous osmotic pressure exerted therein, and it is shown that in the case of yeast the osmotic pressure may be reduced by the action of hypertonic solutions of certain salts to such an extent as to destroy the power of resisting the influence of cold.—New nebulæ discovered at the Paris Observatory, by M. G. Bigourdan.—Observations of Hall's comet 1901(*a*) at the Rio de Janeiro Observatory, by M. H. Morize.—Solar observations at the Lyon Observatory during the first quarter of 1901, by M. J. Guillaume.—On the conjugate nets of orthogonal and